Arsenic Background, Associated Elements and Factors Controlling Mobility

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This presentation includes representative arsenic multimedia background concentrations, mineralogy and controls on arsenic mobility with case histories illustrating these controls. There is a rich history of background arsenic concentrations in most media that are readily sampled in the environment. These background values are strongly related to their origin but the physiochemical conditions where they originate are generally poorly described in tabulations from the literature. Background arsenic concentrations can be used to determine distribution, attenuation and bioaccumulation coefficients but the site-specific conditions within which the background concentrations were determined and for which one is interested need to be carefully evaluated before their use.

Arsenic naturally occurs as a major element in hundreds of minerals and is associated as a minor or trace element in hundreds of additional minerals. Fortunately, most of these involve sulfide and sulphosalt minerals or iron oxydroxide/oxide phases. This considerably simplifies the geochemical conditions one requires to estimate arsenic mobility and arsenic concentrations. From the above mineralogical relationships it is obvious that pH and closed-cell oxidation reduction potential measurements are required field measurements. Unfortunately, most regulatory data requirements collect laboratory instead of field pH values and dissolved oxygen instead of ORP values.

Ongoing geochemical research on arsenic has lead to the quantification of arsenic adsorption onto iron oxyhydroxide/oxide phases under natural conditions involving multiple competing ions. The specific rank of arsenic speciation with respect to commonly associated dissolved metals and other common ions has been developed along with the total adsorption capacity of iron oxyhydroxide/oxide phases. The kinetics of most of these reactions is generally very rapid, commonly less than a few seconds to a few hours, therefore unlike manganese, kinetics is not usually an issue. Current research defines the actual adsorption mechanisms and range of irreversible sorption characteristics under oxidizing conditions but not the range of probable arsenic release under reducing conditions. Reducing conditions needs to be considered in the TCLP protocol for landfill disposal of arsenic adsorbed to iron oxyhydroxide.

Arsenic Background and Associated Elements Controlling Mobility in Groundwater

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Arsenic in Igneous Rocks (mg/kg)

Average 1.5, Range 0.2-13.8, Adriano, 1986

Means 1 to 4

Overall Range 0.06 to 113

Sediments/Sedimentary Rocks/Metamorphic Rocks (mg/kg)

	Mean	SD	Range	
Fresh Water Sediment	1.1			B,1998
Ocean Sediments	33.7	46.7	<0.4-455	B&J, 1973
Shale	14.5	13.8	0.3-500	“
Slate	18.1	16.5	0.1-143	“
Sandstone	4.1	4.7	0.6-120	“
Quartzite	5.5	2.4	2.2-7.6	“
Limestone/Dolomite	2.6	3.0	0.1-20	“
Schist	1.1	1.8	0.0-18.5	“
Gneiss	1.5	1.3	0.5-4.1	“
Phosphorites	41	12.5	3.4-100	“
Iron Formations	45		1.0-2,900	“

Soils (mg/kg)

World Normal Soils Mean 7.2	Range <0.1-97	S&B, 1984; A, 1986; ASTM, 1995
Median 6.0	Range 0.1-40	H, 2000
Geometric Mean 5.2	Range <0.1-97	B, 1998
Bog/Peat Soils Mean 13.4	Range 2-36	B&J, 1973
Standard Deviation 9.4		
Near Arseniferous Deposits Mean 126	Range 2-8,000	B&J, 1973
Standard Deviation 167		

Water (μg/L)

	Mean	SD	Range	
Rain & Snow	1.44	2.17	0.01-13.9	B&J, 1973
Streams, Rivers, Lakes	3.08	5.42	<0.002-0.59	W, 1988
Streams			0.02-264	W, 1988
Lakes			0.38-1,000	W, 1988
Oceans	2.57	1.98	0.006-11.2	B&J, 1973
Groundwater	17.9	13.9	0.01-800	“
Travertine Springs	304	233	30-500	“
Springs, Volvanics	22,200	34,800	120-37,500	“
Hot Springs	2,090	2,650	0.2-40,000	“
Mine Waters			3.0-400,000	“

Arsenic Minerals

	N	**%**
Native Arsenic (As)	1	
Arsenides (X As)	39	14
Sulfides (X AsS)	64	23
Arsenites (X AsO_3Y)	26	9
Arsenates (X AsO_4Y)	147	53

Arsenides (X As)

X	N	%
Ni	9	21
Cu	6	14
Fe	5	12
Pd	5	12
Sb	4	10
Co	4	10
Se	3	7
Pb	2	5
Ru	2	5

Ag, Bi - 1 each

Sulfides (X AsS)

X	N	%
Sb	22	21
Pb	20	18
Cu	14	13
Tl	9	8
Ag	8	8
Fe	6	6
REE (Ru)	6	6
Hg	4	4
Co	2	2
Ni	2	2

Na, Te, Zn, Sn, Se, Bi - 1 each

Arsenic in Common Sulfides

Pyrite	5%
Galena	1%
Sphalerite	1%
Marcasite	0.78%
Chalcopyrite	0.166%
Pyrrhotite	0.015%

Arsenites (X AsO_3Y)

X	N	%
Mn	9	17
Pb	9	17
Fe	6	11
Pb	6	11
Ca	5	9
Cl	5	9
Mg	4	8
Zn	4	8
Si	4	8
Cu	3	6

Sb, Na, K, F - 1 each

Y = (OH)

Arsenates (X AsO_4Y)

X	N	%
Ca	53	16
Fe	42	13
Zn	34	10
Cu	29	9
Mn	26	8
Pb	26	8
Mg	22	7
UO_2	13	4
Cl	10	3
SO_4	9	3
PO_4	9	3
Co	6	2
Sb, Bi, F	5	2
Ni, Ba, Sr	4	1
Si, Mo, REE	3	1
Ti, Y, B, Cd, V	1	0

Y=both (H_2O) and (OH)

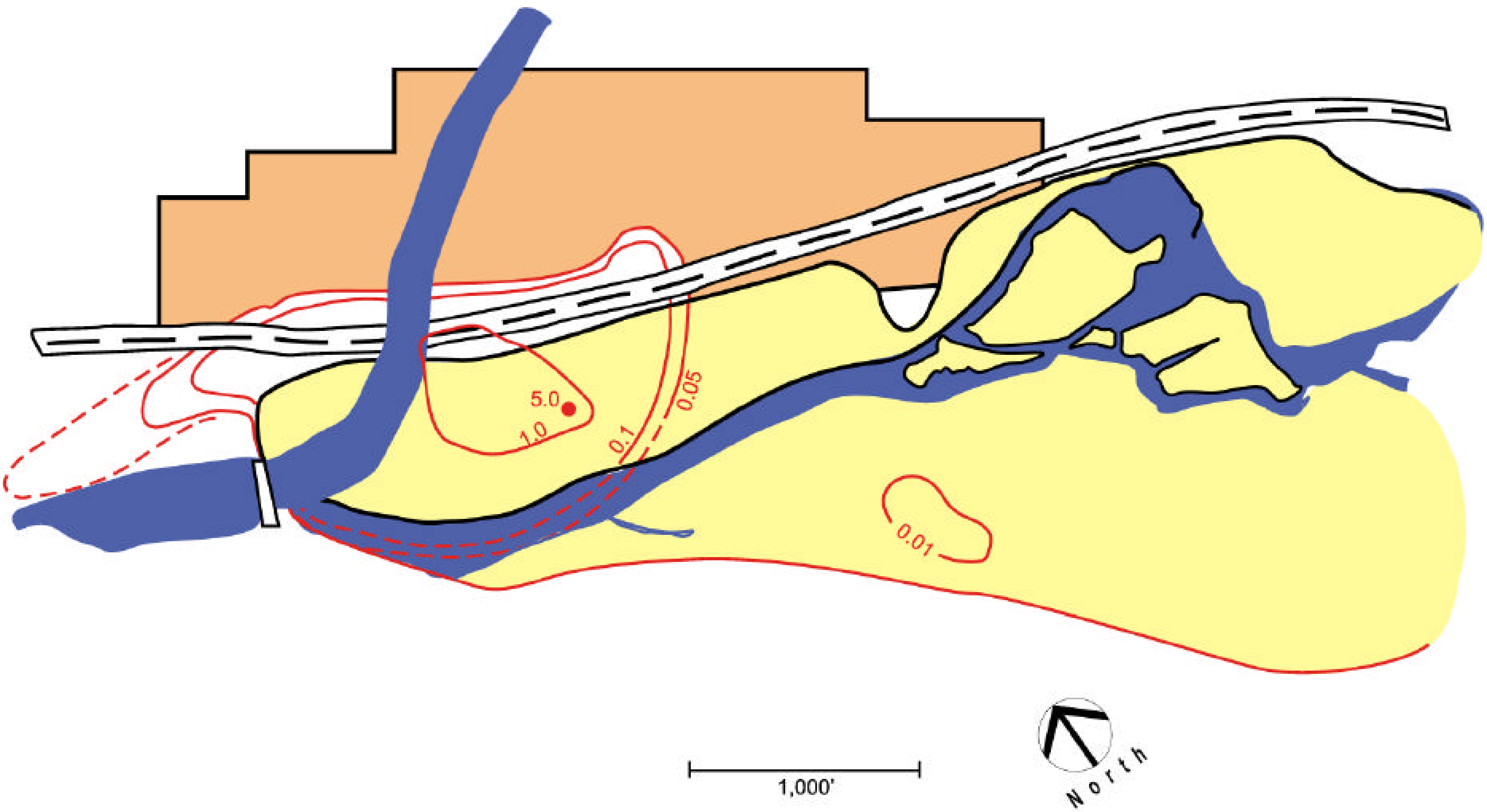
Arsenic Mineralogy

Arsenides	Ni>Cu>Fe = PD>Sb = Co>Se>Pb
Sulfides	Sb>Pb>Cu > Tl>Ag>Fe = REE>Hg
Arsenites	(OH) = Mn = Pb>Fe>Ca = Cl>Mg = Cu=Zn=Si
Arsenates	(H2O)>(OH)>Ca>Fe>Zn>Cu>
	Mn=Pb>Mg>UO_2>Cl>SO_4=PO_4>Co>Sb=Bi=F

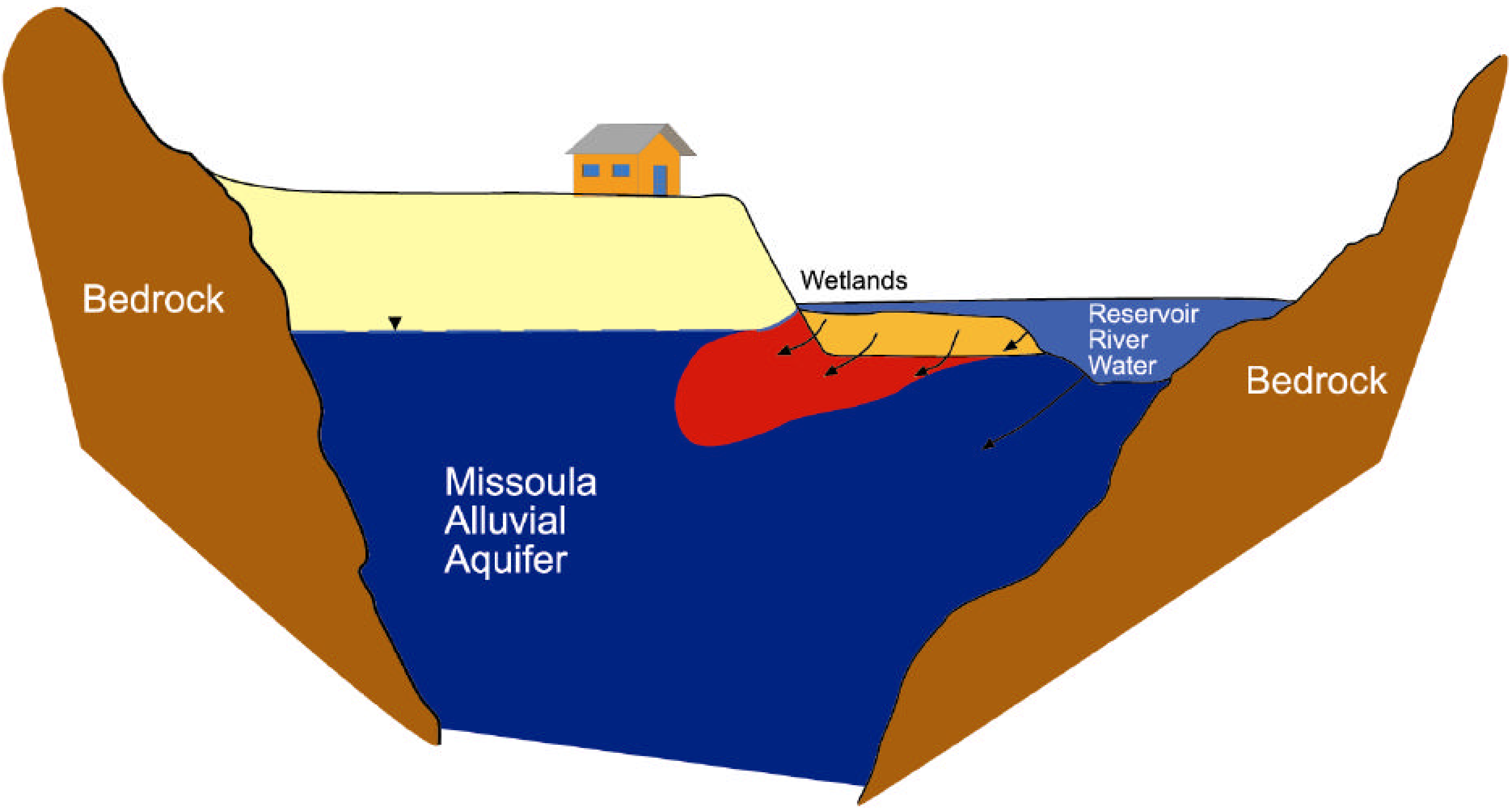
Zykaite

$$Fe_4^{+3}(AsO_4)_3(SO_4)(OH) \bullet 15H_2O$$

Milltown Reservoir
As



Milltown Tailings



Relative Competitive Adsorption

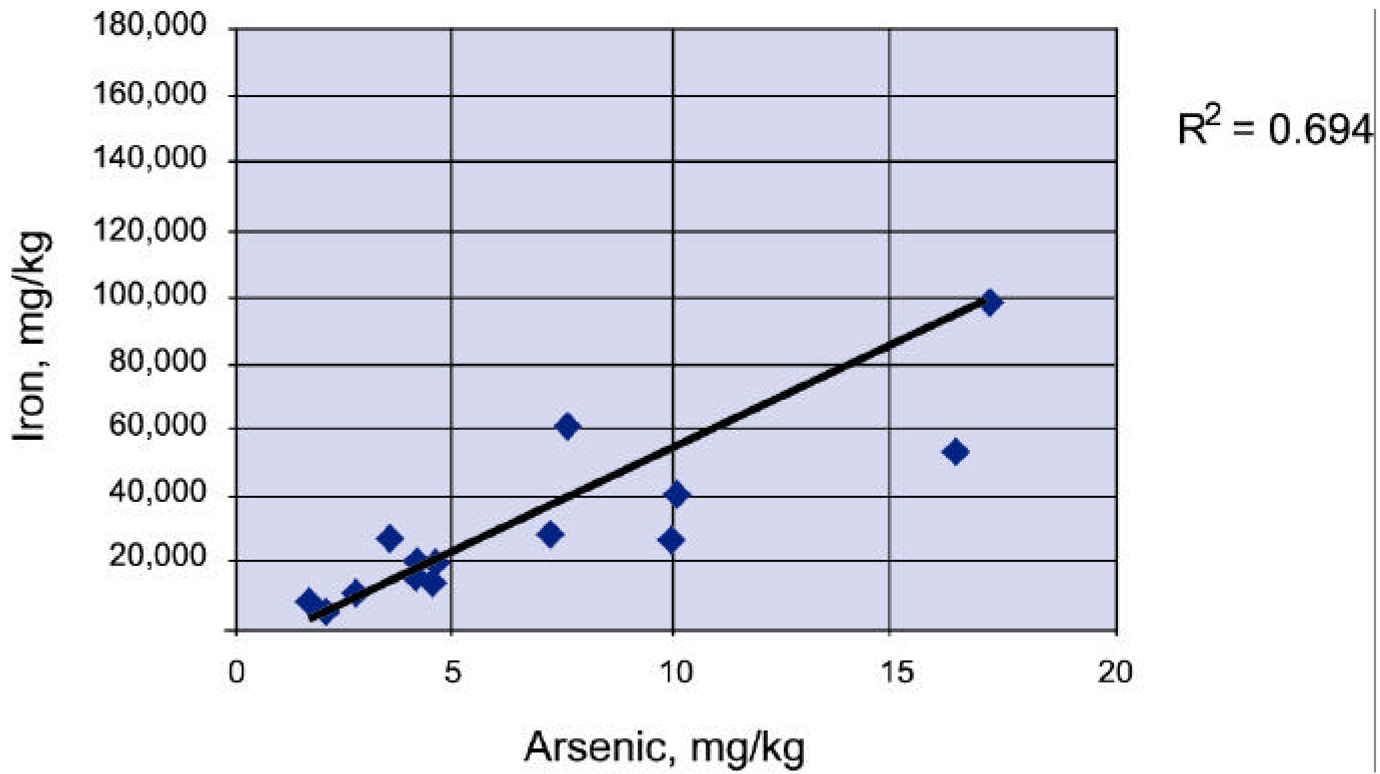
Ferric-Oxyhydroxide, pH 6.5, Atmospheric Conditions

$PO_4 > AsO_4 > SeO_3 > SiO_2 > MoO_4 >>$

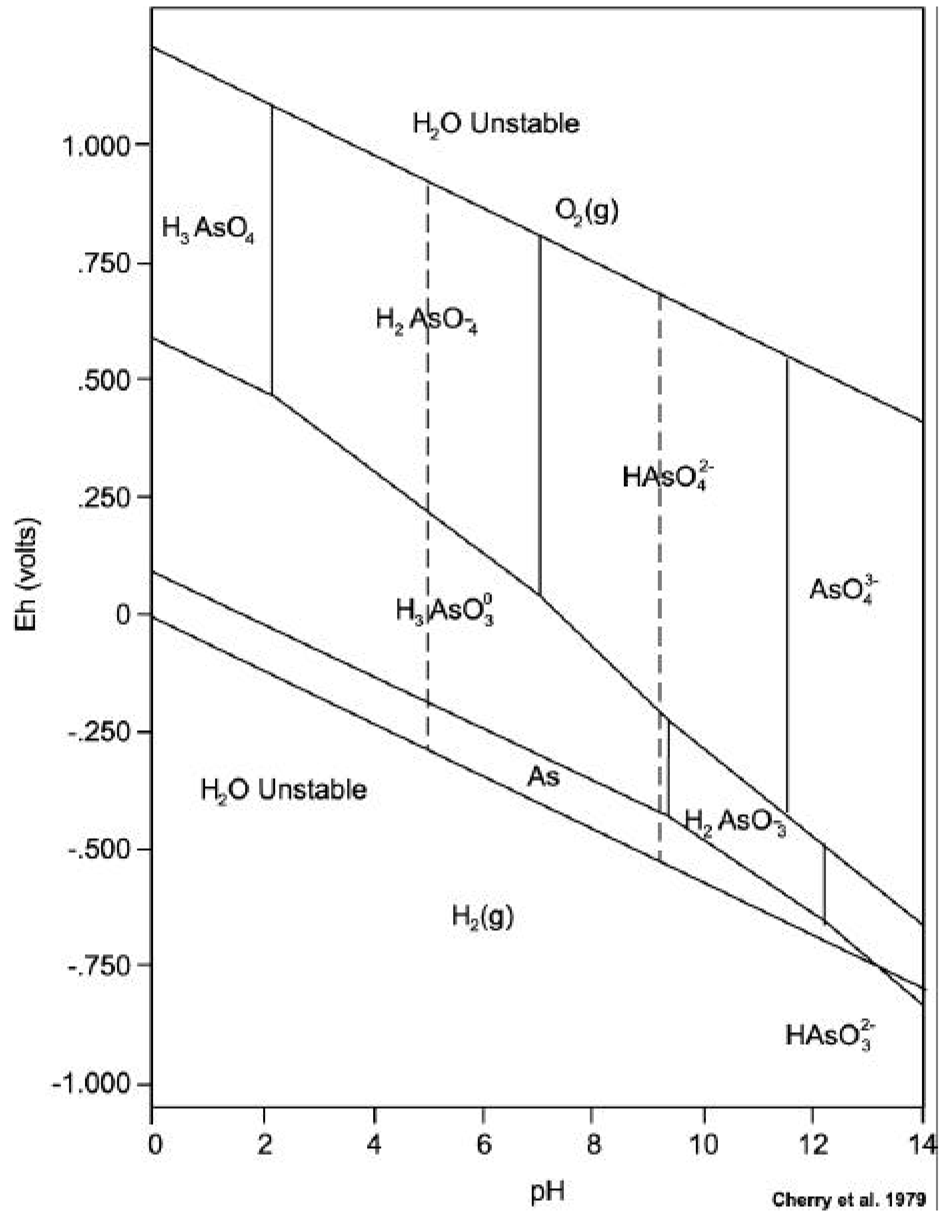
$SO_4 > SeO_4 >>$

Cl

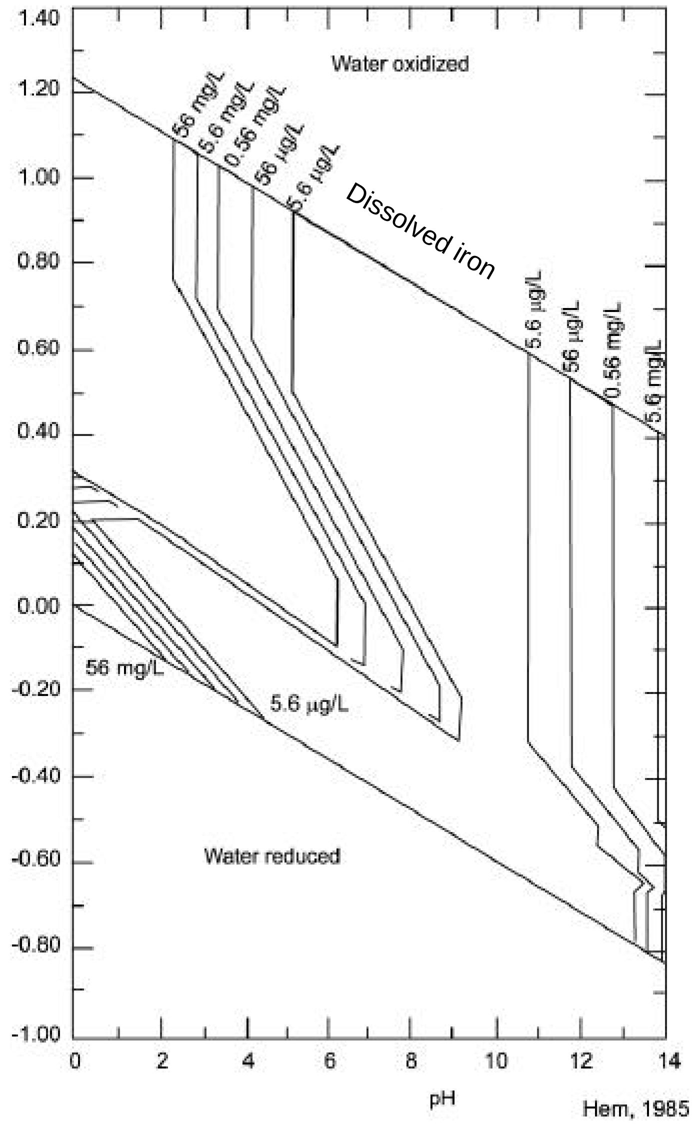
Iron vs Arsenic
Sediments in Crumpton Creek



As-Water

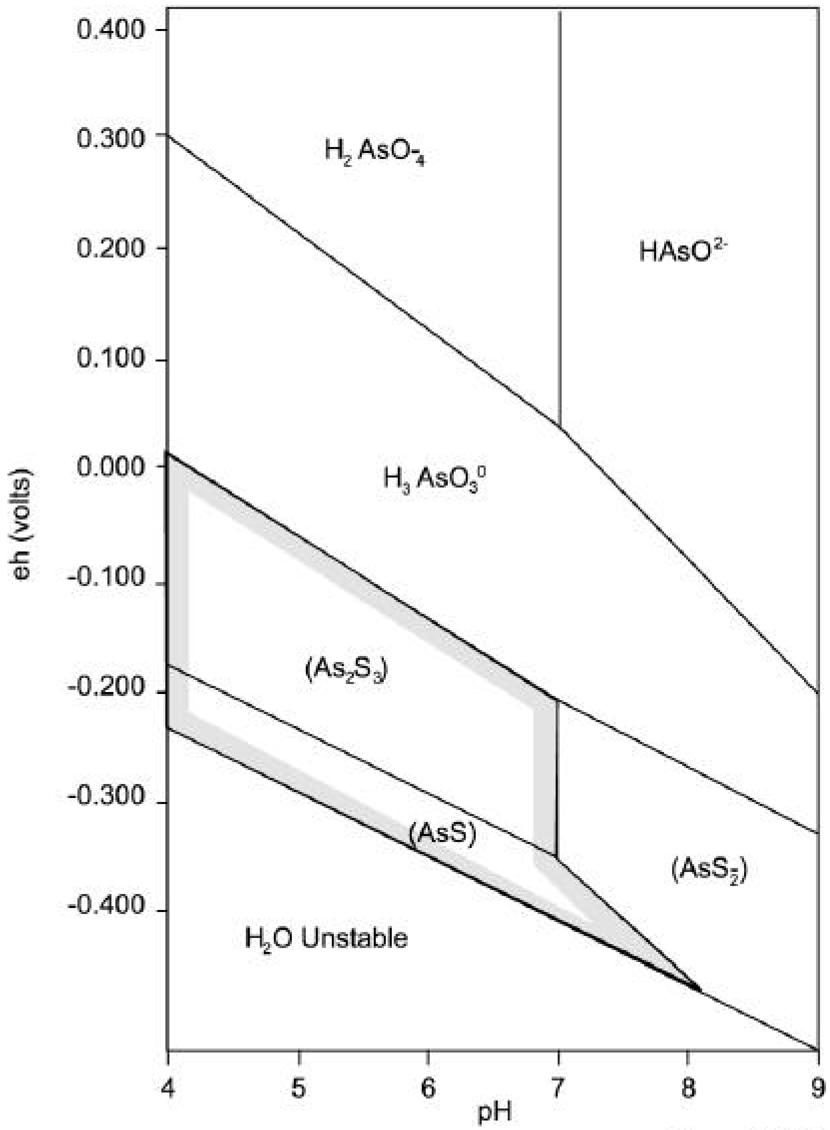

H$_2$O Unstable
O$_2$(g)
H$_3$AsO$_4$
H$_2$AsO$_4^-$
HAsO$_4^{2-}$
AsO$_4^{3-}$
H$_3$AsO$_3^0$
As
H$_2$AsO$_3^-$
H$_2$O Unstable
H$_2$(g)
HAsO$_3^{2-}$
Eh (volts)
1.000
.750
.500
.250
0
-.250
-.500
-.750
-1.000
0
2
4
6
8
10
12
14
pH
Cherry et al. 1979

Fe-S-Water



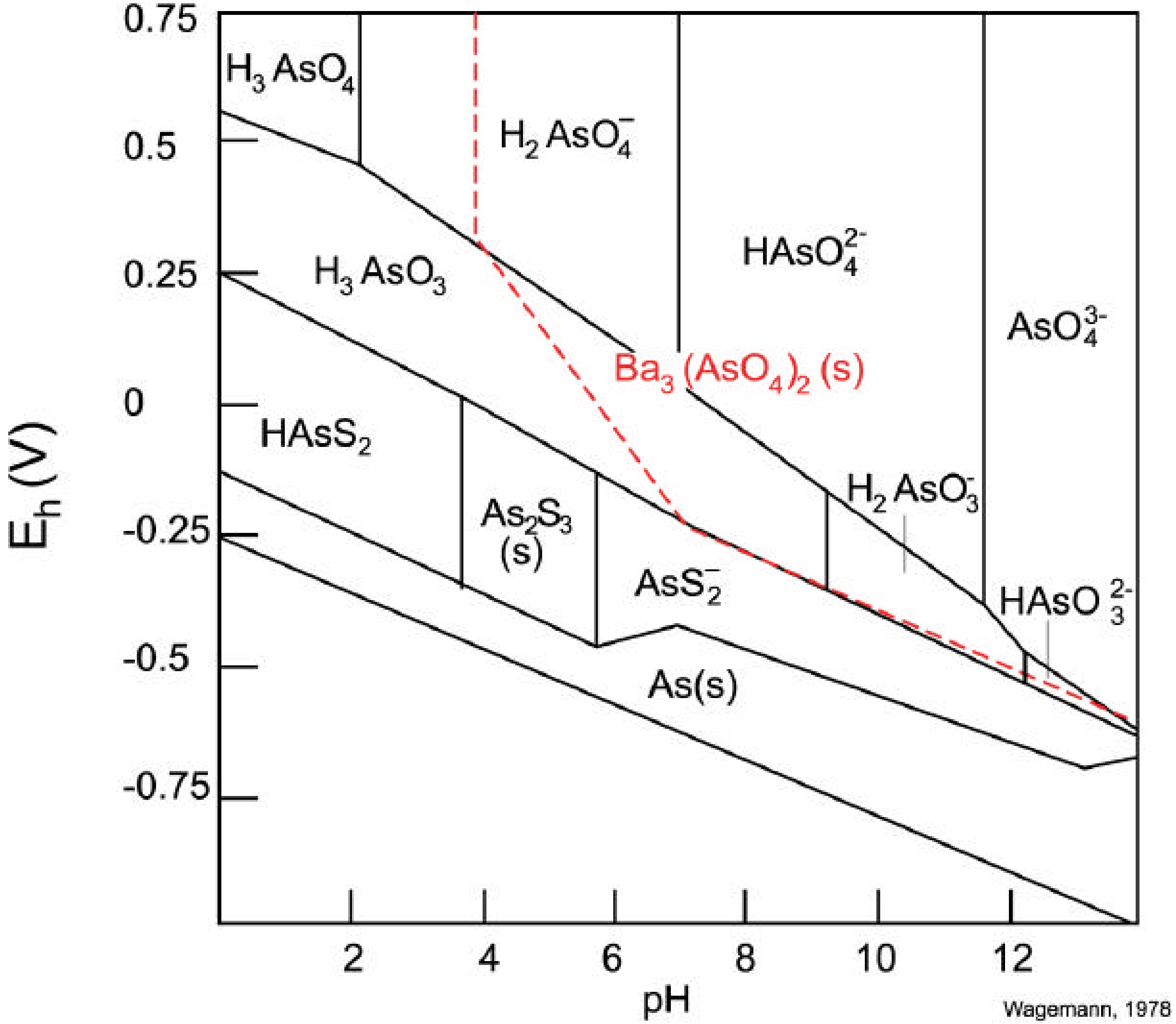
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
-0.20
-0.40
-0.60
-0.80
-1.00
Water oxidized
56 mg/L
5.6 mg/L
0.56 mg/L
56 μg/L
5.6 μg/L
Dissolved iron
5.6 μg/L
56 μg/L
0.56 mg/L
5.6 mg/L
56 mg/L
5.6 μg/L
Water reduced
0
2
4
6
8
10
12
14
pH
Hem, 1985

As-S-Water



Cherry et al. 1979

Ba-As-S-Water



0.75
0.5
0.25
0
-0.25
-0.5
-0.75
E_h (V)
H_3AsO_4
$H_2AsO_4^-$
$HAsO_4^{2-}$
AsO_4^{3-}
H_3AsO_3
$Ba_3(AsO_4)_2$ (s)
$HAsS_2$
As_2S_3 (s)
AsS_2^-
$H_2AsO_3^-$
$HAsO_3^{2-}$
As(s)
2
4
6
8
10
12
pH
Wagemann, 1978

Lead ThioArsensite
PbAsS(SH)(OH)